

A24

1 439 828

## PATENT SPECIFICATION

(11) 1 439 828

- (21) Application No. 18498/73 (22) Filed 17 April 1973  
 (23) Complete Specification filed 25 March 1974  
 (44) Complete Specification published 16 June 1976  
 (51) INT CL<sup>2</sup> C04B 33/04  
 (52) Index at acceptance C1A M11 M9  
 (72) Inventor BARBARA SUSAN NEUMANN



## (54) ORGANOPHILIC CLAY MINERAL DERIVATIVES

- (71) We, LAPORTE INDUSTRIES LIMITED, a British Company of Hanover House, 14 Hanover Square, London, W.1, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—
- This invention relates to clay mineral derivatives and particularly to organophilic derivatives thereof.
- Organophilic derivatives of sodium bentonite, for example Wyoming bentonite, are known. Such products may be produced by exchanging the sodium ions of the bentonite with organic cations which organic cations may be supplied, for example, by onium compounds. Where the sodium bentonite contains exchangeable cations other than sodium it is known to exchange those other ions, or some of them, with sodium ions before, in turn, replacing the sodium ions with cations derived from onium compounds. Thus it has hitherto been considered desirable, not only to use sodium bentonite as a starting material in the manufacture of organophilic derivatives, but also to render the sodium bentonite substantially homoionic before attempting to replace the cations of the sodium bentonite with cations derived from onium compounds. The term "onium compound" is used herein to mean organic ammonium compounds, and isologues thereof, having the general formula  $R_nX_m^+B^-$  wherein R is a organic radical and the element X is in its highest possible positive valency state. n is a number at least equal to 1 and m is a number at least equal to 0, the sum of n and m equalling one less than the highest possible valency of element X. B<sup>-</sup> is an anion for example, hydroxyl or chloride. The term "onium cation" is used herein to mean a cation of the above identified compounds.
- In a paper published in the American Mineralogist Volume 44 pages 1230 to 1236 G. L. McAtee describes an investigation into the production of organophilic derivatives by ion exchanging organic cations onto Wyoming bentonite and hectorite. The results of the investigation indicate that sodium ions are replaced by organic cations more readily than calcium cations which in turn are replaced more readily than magnesium cations. McAtee also describes experiments showing that if organophilic derivatives derived from sodium bentonite on one hand and from sodium bentonite in which the sodium ions have been almost completely replaced by calcium and magnesium ions on the other hand, are washed with distilled water, the former material retains almost all of its organic cations whereas the latter material loses a substantial quantity of its organic cations.
- The McAtee paper therefore teaches that the presence of calcium or magnesium ions on a clay mineral to be used as a starting material for the preparation of organophilic materials is disadvantageous.
- There is some difficulty in ion exchanging calcium ions with sodium ions so as to convert a calcium containing clay mineral into the homoionic sodium form hitherto considered as desirable. One of the most effective methods of conducting such ion exchange is by the use of ion exchange resins. Such a method would achieve substantially complete replacement of the calcium cations by sodium cations but is expensive to use on a commercial scale. Ion exchange can be carried out more economically by contacting the clay mineral with an inorganic compound containing sodium ions combined with anions which form insoluble compounds with the exchangeable calcium ions of the clay mineral such as sodium carbonate, but in practice this method does not enable a satisfactory organophilic derivative to be produced from the resulting sodium-containing product. For these reasons it has not hitherto been thought possible to utilise clay mineral containing a substantial proportion of calcium cations as a starting material for an organophilic clay mineral derivative on a practical commercial scale.
- The present invention relates to the use of clay minerals containing a substantial proportion of calcium ions, for example a major proportion of the exchangeable cations, as

Best Available Copy

- starting materials in the production of organophilic clay mineral derivatives. According to one aspect the invention resides in the use of magnesium compounds, in contrast to 5 McAtee's teaching, in conjunction with sodium compounds in treating such starting materials so as to make them suitable for use in the manufacture of organophilic derivatives.
- Accordingly the present invention provides 10 a process for the production of an organophilic clay mineral derivative comprising taking a clay mineral, containing calcium cations as a major proportion of the exchangeable cations in the clay mineral, treating it in the presence of water with one or more inorganic compounds containing sodium cations and anions which form water-insoluble salts with calcium, and a suitable minor proportion of 15 one or more alkaline magnesium compounds, to exchange sodium and magnesium cations for calcium cations of the clay mineral, and treating the ion exchanged clay mineral with one or more onium compounds to exchange 20 onium cations for said sodium, magnesium and remaining calcium cations.
- A suitable minor proportion of alkaline 25 magnesium compound which may be used in the practice of this invention will depend on the particular embodiment of the invention being practised. The proportion will generally be below 5%, and at least 0.2% based on the weight of the clay mineral. Preferably the proportion of magnesium compound used is from 0.5% to 3% based on the dry weight 30 of the clay mineral.
- The proportion of the compound containing 35 sodium cations is preferably from 4% to 10%, based on the dry weight of the clay mineral. Preferably the compound containing sodium cations is sodium carbonate and the alkaline magnesium compound is magnesium oxide, magnesium carbonate or magnesium hydroxide. The proportion of the onium compound is preferably at least equivalent to the 40 cation exchange capacity of the clay mineral for example up to 20% in excess of the cation exchange capacity of the clay mineral.
- Preferably the onium compound is a suitable 45 organic ammonium compound. Preferably the ammonium compound has at least one organic radical having a carbon chain of at least 10 particularly preferably at least 18, for example even up to 30, 40 or 50 carbon atoms. The reason for such preference is not related to the ease of exchange of the ammonium cation onto the clay mineral which is not affected by the precise composition of the ammonium cation to be exchanged, but is related to the effectiveness of the resulting 50 organophilic clay mineral derivative in use in greases and like media.
- The ammonium compounds may be derived 55 from the class of compounds which includes the salts (including quaternary salts) of primary, secondary and tertiary amines, includ-
- ing mono-, di-, tri-, and poly-amines, aliphatic, aromatic, cyclic and heterocyclic amines and substituted derivatives thereof. Mono- or poly-valent compounds which are of particular value in the practice of the present invention are the "Ethomeens" (Armour and Company). The word "Ethomeen" is a Trade Mark. These compounds may be regarded as tertiary amines having a single alkyl group and two polyoxyethylene groups attached to the nitrogen atom. Similarly the so-called "Ethoduomeens" (Armour and Company) are also of value. The word "Ethoduomeen" is a Trade Mark.
- Specific examples of suitable organic ammonium cations are dimethyl dioctadecyl ammonium, trimethyl octadecyl ammonium, octadecyl ammonium, dioctadecyl morpholinium, 1-propyl 2-octadecyl imidazolinium, bis(-2-hydroxyethyl) octadecyl ammonium, and dimethyl benzyl lauryl ammonium. These 60 may be used singly or in combination.
- A suitable clay mineral for use in this invention is calcium montmorillonite. This mineral is widely available. Preferably the clay mineral has a cation exchange capacity of from 0.7 to 1.1 m.e/g.
- In carrying out the process of the present invention it is important to achieve intimate contact between the clay mineral and the sodium and magnesium-containing compound or compounds used and for this the presence of water is necessary. Suitably the clay mineral is treated in the form of a damp clod, with the compound or compounds providing sodium and magnesium cations. Preferably the clay mineral treated contains from 28 to 40% by weight of water. Preferably intimate contact is achieved by first mixing the clay mineral with the compound or compounds providing sodium and magnesium cations and then extruding the mixture. The clay mineral is then advantageously dried at a temperature not exceeding 400° C to a water content of 4% to 22%.
- The resulting clay mineral derivative may be treated with the onium compound in the form of a dispersion of the clay mineral derivative in water, preferably at a concentration of 1% to 12%. The clay mineral may be dispersed by, for example, mixing the suspension, at high shear, for a sufficient time to reduce the particle size therein to smaller than 2 micrometer average equivalent Stokes diameter. The dispersion of the clay mineral may be conducted at ambient temperature. The onium compound or compounds may also be dispersed in water at, for example 1 to 6% concentration and then the two dispersions may be mixed. Preferably the two dispersions are mixed at an elevated temperature of, for example, from 60 to 100° C and are maintained at an elevated temperature for a period of time sufficient to allow the ion exchange to take place. Preferably the two 65 70 75 80 85 90 95 100 105 110 115 120 125 130

suspensions are stirred for from 5 to 30 minutes after mixing. Thereafter the organophilic clay mineral derivative resulting from the ion exchange with the onium compound is preferably filtered and washed to free it from the inorganic exchangeable cations of the clay and the anion of the onium compound used. The clay mineral derivative is then preferably dried, for example, to a water content of 2 to 3%. It is then ready for incorporation in organic media.

The organophilic products of this invention are suitable for use in organic solvent systems such as white spirit and their purpose is to stiffen the system. They are useful, in particular, in paint systems.

When the organic solvent is or contains a substantial quantity of polar solvent such as, for example, ethanol the effect of the organophilic clay mineral derivatives is particularly advantageous. Where the organophilic derivative is to be used in a medium not containing a polar solvent, the organophilic derivative is preferably treated with such a solvent before incorporation in the medium. A suitable quantity of polar solvent is from 0.5 to 1.0 g/g of the dried organophilic clay mineral derivative.

In order that the invention may be more readily understood examples thereof will now be specifically described. Certain examples not according to the invention will also be specifically described for the purposes of comparison. Examples 3—9 are according to the invention and Examples 1 and 2 are not according to the invention and are inserted for comparative purposes.

The following procedure was used in carrying out all the examples.

The clay mineral, in the form of a wet clod, of 34—36% by weight moisture, was, where the particular example required the presence of one or more of sodium carbonate and magnesium oxide, extruded with 9% based on the dry weight of the clod of sodium carbonate and/or 2% based on the dry weight of the clod of magnesium oxide (Taycrest T3 made by Taycrest Company Limited). "TAYCREST" is a trade mark. The ex-

truded clod mixture (or the clod itself, where appropriate), was dried and milled. The resulting milled product was made up to a 4% by weight dispersion in water by mixing under conditions of high shear for 15 minutes with distilled water at ambient temperature. The dispersion was heated to 80° C. A paste of 75% concentration of dimethyl dioctadecyl ammonium chloride in isopropanol, which is available under the Trade Mark "ARQUAD 2HT", was dispersed in distilled water at 6% concentration by weight and heated to 80° C to 90° C.

The two dispersions were mixed in proportions to give the required quantity of organic ammonium cation indicated, and stirred at 80° C for 10 minutes. The resulting solid product was filtered and washed on the filter with distilled water until chloride free. The filter cake was dried at 80° C to 2 to 3% water as shown by thermogravimetric analysis.

The resulting organophilic product was mixed with a mixture of white spirit and ethyl alcohol. 6g samples of organophilic product were used and the quantity of white spirit and ethyl alcohol was 68g per sample, the quantity of ethyl alcohol varying as indicated in Table I.

Mixing was conducted by first adding the white spirit, mixing for 5 minutes under high shear conditions, adding the ethyl alcohol and further mixing under high shear conditions for 1 minute. Some of the samples were tested using a cone micropenetrometer, of 15.8g weight and solid angle of 90°, immediately. All the samples were then passed through a triple roll mill twice and tested with the cone penetrometer. The results are expressed in  $10^{-4}$  metres penetration. For guidance a penetration value of 200—350  $\times 10^{-4}$  m. indicates a soft grease-like body of dropping consistency, a value of 50—200 a body similar in consistency to shoe polish, and a value below 50 a stiff grease-like body.

The results of these tests are summarised in Table I, which also includes some details of the conditions used in carrying out the various examples.

50

55

60

65

70

75

80

85

90

95

TABLE I

Ex. No.	Type of calcium montmorillonite clay	Extruded with wt % of		Exchangeable cation content of extruded dried product me '100g			
		Na <sub>2</sub> CO <sub>3</sub>	MgO	Na <sup>+</sup>	Ca <sup>++</sup>	Mg <sup>++</sup>	Ca <sup>++</sup> + Mg <sup>++</sup>
1	Surrey blue clay	—	—	6	84	5	89
2	Surrey blue clay	9%	—	91			4
3	Surrey blue clay	9%	2%	79			16
4	Surrey blue clay	9%	2%	79			16
5	Surrey blue clay	9%	2%	87			8
6	Surrey blue clay	9%	2%	87			8
7	Kent clay	9%	1.5%	78			10
8	Kent clay	9%	1.5%	78			10
9	Kent clay	9%	1.5%	78			10

TABLE I (Continued)

Ex. No.	Organic Ammonium cation me. g dried clay mineral	$C_2H_5OH$ g/g clay deriv. (dried)	Penetration value $10^{-4} m$	
			before 3-roll milling	after 3-roll milling
1	0.85	0.33	~	~
2	0.85	0.33	395	145
3	0.85	0.33	349	86
4	0.85	1.00		57.5
5	0.85	0.33		73
6	0.85	1.00		60
7	0.70	0.33		77
8	0.70	0.66		47
9	0.70	1.00		31

- Surprisingly products of this invention although based on naturally occurring calcium montmorillonite can be comparable to products based on sodium bentonite. An organophilic product based on sodium bentonite (Wyoming Bentonite) available under the Trade Mark Volclay but otherwise made, as described in the examples, containing 0.70 organic ammonium cation/g clay mineral and made up, for testing to include 0.33 g ethyl alcohol/g clay mineral, gave a penetration value after 3 roll milling of 34, and a commercial organophilic product available under the Trade Mark Bentone 34, also based on sodium bentonite, gave penetrometer test results equivalent to those of the Volclay derived product. There is a correlation between the rheological properties of a suspension of the clay in water before being treated with onium compound, and the inclusion of a magnesium compound and it is possible that the effect of the magnesium compound in increasing the degree of dispersion of the clay, as shown by the improved rheological properties of the

suspension is responsible for the improvement in the effectiveness of the organophilic product. This is a theory and the invention described and claimed herein is not limited thereby. Table II gives the plastic viscosity of a 6% suspension of clay mineral, after extrusion, if carried out, and drying, but before treatment with ammonium compound.

The plastic viscosity was measured on a Ferranti-Shirley Cone and Plate Viscometer and is expressed in centipoises.

30

35

Table II.

Ex. No. Plastic Viscosity

1	1
2	4
3	8
4	8
5	10
6	10
7	10
8	10
9	10

The results appear to indicate to a limited extent, an interrelationship between the rheological properties of the clay mineral and the use of the magnesium compounds.

5      **WHAT WE CLAIM IS:—**

1. A process for the production of an organophilic clay mineral derivative comprising taking a clay mineral, containing calcium cations as a major proportion of the exchangeable cations in the clay mineral, treating it in

10     the presence of water with one or more inorganic compounds containing sodium cations and anions which form water-insoluble salts with calcium, and a suitable minor proportion of one or more alkaline magnesium compounds, to exchange sodium and magnesium cations for calcium cations of the clay mineral, and treating the ion exchanged clay mineral with one or more onium compounds (as hereinbefore defined) to exchange onium cations for said sodium, magnesium and remaining calcium cations.

15     2. A process as claimed in claim 1 wherein the clay mineral is calcium montmorillonite.  
25     3. A process as claimed in claim 1 or 2 wherein the compound containing sodium cations is sodium carbonate.  
30     4. A process as claimed in any preceding claim wherein the alkaline magnesium compound is magnesium oxide, magnesium hydroxide or magnesium carbonate.

35     5. A process as claimed in any preceding claim wherein the clay mineral is treated with from 4% to 10% based on the dry weight thereof of the compounds containing sodium cations.

6. A process as claimed in any preceding claim wherein the clay mineral is treated with from 0.5 to 3.0% based on the dry weight thereof of the magnesium compound.

40     7. A process as claimed in any preceding claim wherein the clay mineral is in the form of a wet clod containing from 28% to 40% by weight of water.

45     8. A process as claimed in any preceding claim wherein the clay mineral is treated with the compound containing the sodium cations and the alkaline magnesium compound by being extruded in admixture with the said compounds.

50     9. A process as claimed in any preceding claim wherein the onium compound is an ammonium compound.

55     10. A process as claimed in any preceding claim wherein the onium compound is in a quantity at least equivalent to the cation exchange capacity of the clay mineral.

60     11. A process substantially as described herein with reference to any one of Examples 3 to 9.

65     12. An organophilic clay mineral derivative whenever produced by a process as claimed in any preceding claim.

13. An organophilic clay mineral derivative as claimed in claim 12 in admixture with a polar solvent in an amount of from 0.5 to 1.0 g/g of clay mineral derivative based on the dry weight thereof.

A. N. CALDWELL,  
Chartered Patent Agent,  
Agent for the Applicants.

## **PRODUCTION OF NYLON 6**

**Patent number:** JP62252426  
**Publication date:** 1987-11-04  
**Inventor:** OKADA AKANE; others: 03  
**Applicant:** TOYOTA CENTRAL RES & DEV LAB INC  
**Classification:**  
- **international:** C08G69/16  
- **european:**  
**Application number:** JP19860095781 19860424  
**Priority number(s):**

### **Abstract of JP62252426**

**PURPOSE:** To facilitate the production of nylon 6 of a desired crystalline structure (alpha or gamma-form), by polymerizing a monomer for nylon 6 in the presence of a silicate at a temperature higher than the melting point of the monomer and cooling the product at a specified cooling rate.

**CONSTITUTION:** 100pts.wt. monomer (A) for nylon 6 (e.g., caprolactam) is polymerized in the presence of 0.001-100pts.wt. silicate (B) (e.g., montmorillonite), desirably, swollen with an organic substance (e.g., 12-aminododecanoic acid hydrochloride) at a temperature higher than the melting point of component A (about 220 deg.C), and the product is cooled at a cooling rate  $\leq 4$  deg.C/min from the melting point or above to 160 deg.C or below to obtain a composite of nylon 6 of an alpha crystalline structure with the silicate or cooled at a cooling rate  $\geq 10$  deg.C/min to obtain a composite of nylon of a gamma crystalline structure. This composite is dissolved in a solvent (e.g., m-cresol), and the silicate is removed to obtain nylon of an alpha or gamma crystalline structure.

---

Data supplied from the *esp@cenet* database - Patent Abstracts of Japan

**This Page is Inserted by IFW Indexing and Scanning  
Operations and is not part of the Official Record**

**BEST AVAILABLE IMAGES**

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- BLACK BORDERS**
- IMAGE CUT OFF AT TOP, BOTTOM OR SIDES**
- FADED TEXT OR DRAWING**
- BLURRED OR ILLEGIBLE TEXT OR DRAWING**
- SKEWED/SLANTED IMAGES**
- COLOR OR BLACK AND WHITE PHOTOGRAPHS**
- GRAY SCALE DOCUMENTS**
- LINES OR MARKS ON ORIGINAL DOCUMENT**
- REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY**
- OTHER:** \_\_\_\_\_

**IMAGES ARE BEST AVAILABLE COPY.**

**As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.**